

Cationic Latex Interaction with Pulp Fibers. II. Modification of Sheet Properties by Styrene- Butadiene Latex with Quaternized Amino Groups

B. ALINCE, *Pulp and Paper Research Institute of Canada, Pointe Claire,
Quebec, Canada*

Synopsis

Unbeaten kraft fibers covered with experimental cationic latexes were formed into sheets in which direct fiber-fiber bonds are replaced by polymeric bonds. The effect on sheet properties—breaking length, elongation at break, folding endurance, opacity, and light scattering—was evaluated as a function of latex composition. The composition was altered by either the ratios of styrene to butadiene in the polymer or by mixing soft film-forming and hard nonfilming latex. It is shown that, regardless of latex composition and mechanical properties of the polymeric film, all the latexes can modify the sheet properties to a similar extent, providing that the sheets are heated above the polymer's glass transition temperature. An improvement of tensile strength is accompanied by increased elongation. As a probable mechanism of reinforcement, it is suggested that the polymer acts as a filler of the fiber's surface irregularities, thus providing a larger contact area between fibers and an improved stress transfer between them.

INTRODUCTION

Polymer introduction for the purpose of modifying sheet properties can be conveniently achieved by wet-end addition of latex. However, the selection of an appropriate polymer is often based on experimentation due to a lack of knowledge concerning the expected polymer performance in the formed sheet. The complexity of the system prevents more than a general statement that the properties of the final product depend on the latex quantity, identity, and distribution. At the same level of addition, the latex distribution has been shown^{1,2} to alter considerably the tensile strength of sheet depending on whether the polymer substitutes for or supplements the direct interfiber bonding. A film-forming polymer has been found most effective in improving the coherence of a sheet formed from unbeaten fibers when the fibers were uniformly coated with latex, i.e., when fiber-fiber bonds were replaced with polymeric bonds. Conversely a nonfilming latex deposited uniformly on fibers was most effective in reducing the bonding.

In this report the effect of latex composition on sheet properties is investigated. The composition and consequently the filming properties are altered by either the ratio of styrene to butadiene in the polymer or by mixing soft film-forming and hard nonfilming latexes. All the latexes are cationic in nature in order to facilitate their retention on fibers without any deposition aids. The absence of deposition aids is believed to promote a uniform deposition of latex particles and consequently the substitution of the fiber-fiber bonds by polymeric bonds.

EXPERIMENTAL

Materials

Pulp Fibers. Bleached, unbeaten kraft fiber was washed three times with distilled water in order to remove fines, which were observed to attract the latex preferentially, thus interfering with an even latex deposition.

Latex. Four experimental cationic latexes of different styrene-butadiene content were prepared in the absence of emulsifier by a procedure described elsewhere.¹ The cationic charge was supplied by adding 1% 2-(diethylamino) ethyl methacrylate quaternized with dimethylsulfate to the reaction mixture. Polymerization was carried out at 60°C for 8 hr using H₂O₂ and Fe(NO₃)₃ as initiator. The latex was twice subjected to flash evaporation to remove the unreacted monomers, followed by dialysis for a week. The latexes were reasonably monodisperse with particle size between 120 and 160 nm as estimated from electron microscopy. The ratio of styrene to butadiene was determined from the consumption of bromine by the olefinic double bonds in the styrene-butadiene molecule.³

Methods

Latex Addition and Sheet Formation

An appropriate amount of latex diluted in 100 ml water was added to a fiber suspension (1 g in 400 ml) under slow (90 rpm) paddle stirring. After 30 min, when all the latex had deposited on the fibers, the supernatant was filtered off, and the fibers were transferred to the British standard sheet-forming apparatus. Throughout the whole procedure only distilled water was used. The sheets of basis weight 55 g/m² ± 7% were dried at room temperature and subsequently heated for 5 hr at 105°C. Samples treated with a mixture of soft and hard latexes were also pressed at 10 atm (≈ 1 MPa) and 150°C for 1 hr.

Handsheet Testing

Mechanical Properties. Breaking length, elongation at break, and folding endurance were determined according to the methods described in Tappi Standard T-220.

Optical Properties. Opacity was determined according to Tappi Standard T-425. Reflectance of the sheet backed with white and black background was measured at 545 nm using a Zeiss Elrepho apparatus. The specific light-scattering coefficient expressed on basis weight was calculated from the Kubelka-Munk theory.^{4,5}

Surface Area. This parameter was determined by dynamic nitrogen adsorption from nitrogen-helium mixture utilizing a gas-chromatographic technique in an apparatus described elsewhere.⁶

Water Absorbency. A sample suspended from the arm of a Cahn Electrobalance RG was brought into contact with a water surface and the change in weight due to water penetration was continuously recorded. The sample-water contact was accomplished by raising a container with water until the bottom edge of the sample touched the water surface.

Latex Distribution on Fiber

Wet fiber samples taken from the suspension in the sheet machine were brominated in order to prevent coalescence of the soft latex particles⁷ and were observed by scanning-electron microscope.

RESULTS AND DISCUSSION

The effect of incorporated polymer on the mechanical properties is difficult to predict considering the complexity of the system, which defies a detailed understanding of the mechanisms involved. The method of polymer introduction (before, during, or after the paper-making process) and its form (in solution or as latex) may considerably alter the polymer contribution to the properties of the composite⁸ by affecting the polymer location in the network and its ability to transmit stresses between fibers. Two extreme cases of polymer location may be envisaged: (1) the fiber-fiber bonds are supplemented by additional polymeric interfiber bonds or (2) the direct fiber bonding is substituted by polymeric interfiber bonds.

In a systematic study of polymer-paper composites,⁸ the first case was approximated by impregnating a formed sheet with a nonaqueous polymer solution. Treatment with a variety of polymers showed that the properties of the polymer are directly reflected in the mechanical properties of the sheet. With rubbery polymers, the elongation increases; with brittle polymers, the strength is improved. A sheet impregnation by aqueous latex produces a wider difference in behavior because some of the original bonds are broken by the water and replaced by polymeric interfiber bonds.

It is very difficult to assess the role of the polymer when it is added at the wet-end. The deposition of latex on fibers is controlled by colloidal phenomena, and since the conventional latexes are anionic, they do not deposit on cellulosic fibers without some aid. This usually involves the coagulation of the latex, which results in latex deposition in form of aggregates. Due to the difficulty in controlling aggregate formation, a considerable variability is introduced into the distribution of the polymer on the fibers, which may vary from a complete encapsulation of fibers up to a sparse coverage by large aggregates. It has been shown earlier^{1,2} that the distribution of a given polymer can significantly affect its performance as a binder, which makes a comparison of various polymers if a similar distribution is not ensured rather dubious.

The use of cationic latexes may simplify the situation due to the natural attraction between latex and fiber resulting in a ready deposition. The distribution of latex on the fiber surface can be controlled by affecting the stability of the depositing latex. Stable latex tends to cover the fiber in the form of individual particles, and, depending on its amount, it may completely encapsulate the fiber.² When a sheet is formed from such fibers, a substitution of direct interfiber bonds by polymeric bonds is likely, i.e., the second extreme case mentioned above is approximated.

In this study the effect of latex composition on sheet properties was investigated by depositing stable, cationic latex on unbeaten fibers under conditions that promote full deposition. Four experimental latexes were employed that differed in styrene-butadiene ratio and, consequently, in softness. These deposit fully at pH 6 up to 10% latex addition (on fibers), which is an amount sufficient

to give complete coverage of all fibers with a uniform layer of individual particles. At pH 6 all the latexes are stable according to studies reported earlier,⁹ yet uniform coverage was not achieved with all of them. With increasing butadiene content, the tendency towards aggregation increases, thus changing the uniformity of deposition. However, at 10% latex addition, the fibers appear to be reasonably well covered with any of the latexes, and the substitution of direct interfiber bonds by polymeric bonds therefore seems to be assured.

Two series of experiments were performed. In the first, the four latexes were deposited in amounts of 2, 5, and 10% (on fibers); the sheets were formed; dried at room temperature; and finally heated for 5 hr at 105°C. The heating was found necessary to allow the film-forming latexes to develop their full potential in sheet reinforcement.¹⁰ The characteristics of the employed latexes are listed in Table I.

In the second series, various mixtures of hard latex 100/0 and soft latex 56/44 were employed for the purpose of altering the properties of the polymer. In each case a total amount of 10% latex (on fibers) was used and full deposition was achieved. Although a reasonable fiber coverage was achieved, the latex distribution on the fiber surface varied with the ratio of hard to soft latex. With an increasing amount of soft latex, more small aggregates were observed by the scanning-electron microscope as shown in Figure 1.

Effect of Latex with Different Composition

The properties of sheets formed from bleached, unbeaten kraft fibers treated with 2, 5, and 10% latex of different styrene content and heated at 105°C for 5 hr are shown in Figure 2. The pure polystyrene latex is nonfilming and, probably because of its high glass transition temperature, the heating at 105°C is insufficient to allow the latex particles to deform and coalesce. Therefore, polystyrene prevents contact between fibers, and the properties that depend on such contact gradually deteriorate with increasing latex content. On the other hand, the opacity improves with the increasing separation of fibers, as expected.

The other three latexes containing butadiene are film forming, and, since the heating at 105°C is well above their glass transition temperature, the full potential of providing better contact between fibers can develop. Although the softest latex is most efficient, the small difference in performance of all three latexes prevents any conclusion concerning their relative effectiveness. It is of interest that although the mechanical properties of styrene-butadiene copolymer films may differ considerably with the butadiene content this is not reflected in their performance as binders. Figure 3 shows the load-elongation curves of films formed from the latex alone and heated at 105°C for 5 hr.

The coverage of fibers by polymer quite naturally results in decreased water absorbancy. Figure 4 shows typical examples of relative water absorption rates

TABLE I
Latex Characteristics

Styrene-butadiene ratio	100/0	71/29	63/37	56/44
Average particle radius (nm)	80	80	70	60
Glass transition temp (°C) ^a	100	16	0	-14

^a From L. A. Wood, *J. Polym. Sci.*, 28, 319 (1958).

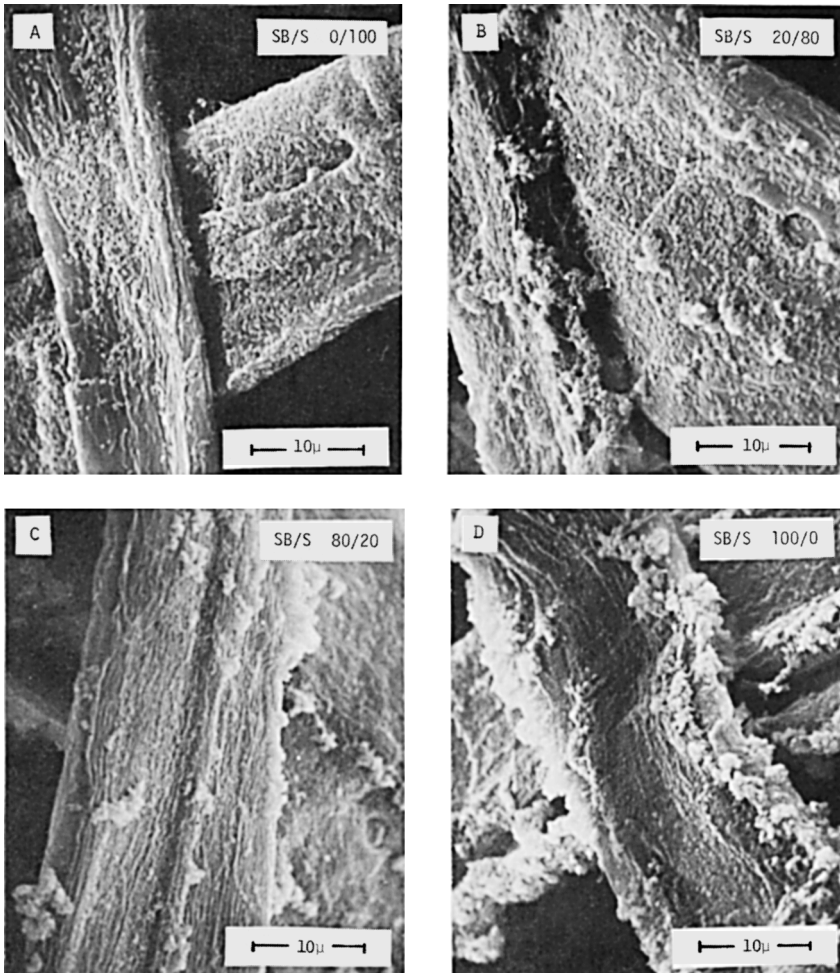
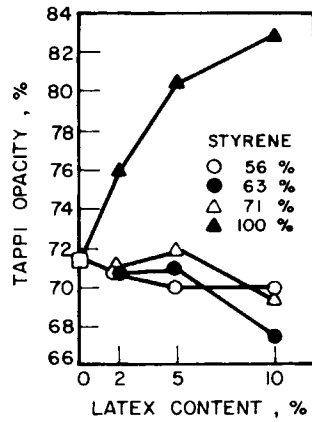


Fig. 1. Latex distribution on pulp fibers treated with various mixtures of soft (SB) and hard (S) latex. The hard latex 0/100 deposits as individual particles (a); with increasing ratio of the soft latex—20/80 (b), 80/20 (c), and 100/0 (d)—deposition as aggregates increases.

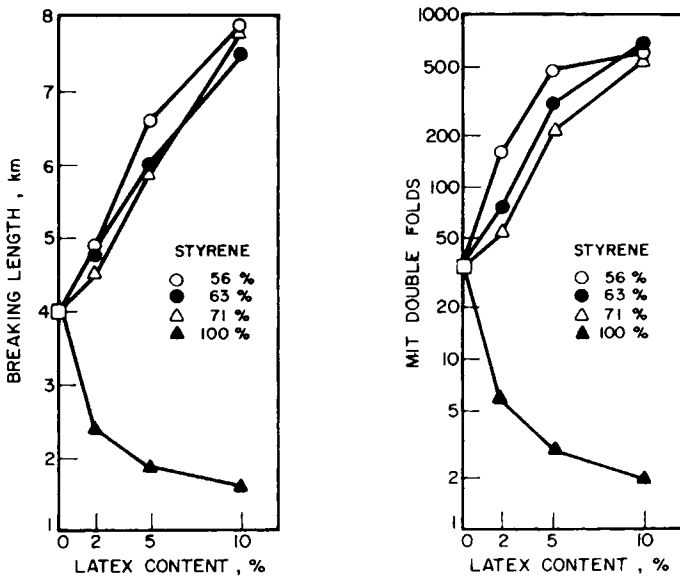
by a control sheet without latex (1) and a sheet containing 10% of filming latex dried at room temperature (2) that was then heated at 105°C for 5 hr (3). The heat treatment apparently allows the polymer film to cover the fibers more effectively.

Effect of Mixtures of Soft and Hard Latex

Figure 5 shows the properties of sheets formed from bleached, unbeaten kraft fibers treated with mixtures of hard polystyrene latex 100/0 and styrene-butadiene copolymer latex 56/44. The total amount of latex is 10% on fibers. The results are shown for sheets dried at room temperature (dashed line) and subsequently at 105°C for 5 hr (solid line). The results from sheets containing 10% hard polystyrene latex heated for 1 hr at 150°C in a press at 1 MPa (≈ 10 atm) are also presented in the figure (as single points). The horizontal lines represent the properties of a control sheet dried at room temperature (dashed line) and



(a)



(b)

Fig. 2. Sheet properties as a function of the amount of latex (2, 5, and 10% on fibers) and its composition (styrene content 56, 63, 71, and 100%). Sheets heated at 105°C for 5 hr.

at 105°C for 5 hr (solid line). The trend in sheet property development with increasing content of hard latex follows the expected behavior. The hard latex acting as a pigment reduces the effectiveness of the film-forming latex as a binder. This is particularly demonstrated in the tensile strength improvement resulting from a heat treatment at 105°C. The temperature is well above the glass transition of the soft polymer and about the same as the glass transition of the hard polystyrene. Therefore, the soft polymer can respond more readily in developing its full potential, and the tensile strength improvement due to heating increases with the content of the soft polymer. However, by increasing the temperature to 150°C and giving a subsequent pressing, the hard polystyrene can approximate the performance of the soft polymer.

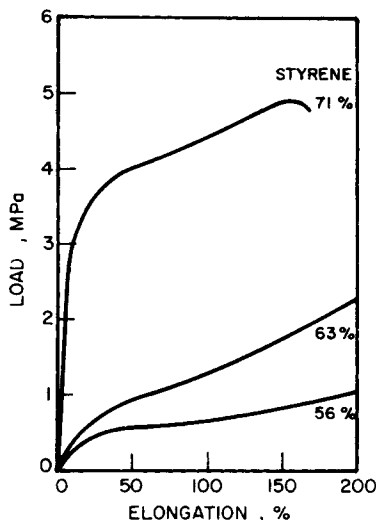


Fig. 3. Load-elongation curves of films formed from latexes of different styrene-butadiene content and heated at 105°C for 5 hr.

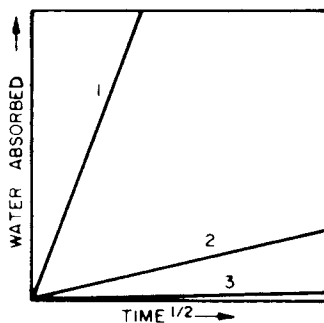


Fig. 4. Typical rates of water uptake by sheets: (1) control without latex, (2) with 10% soft PSB latex dried at room temperature, and (3) same as (2) heated at 105°C for 5 hr.

Mechanism of Sheet Reinforcement

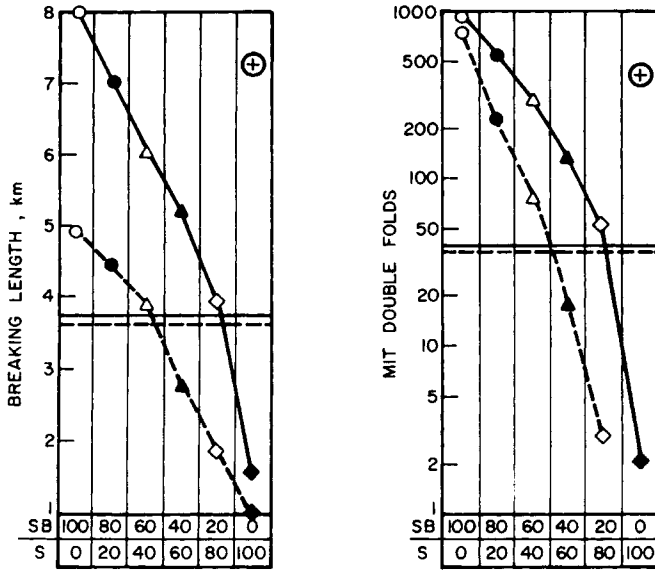
In speculating about the probable role of latex in the sheet reinforcement, a few points should be considered.

First, experiments have been restricted to situations where direct interfiber bonds are substituted by polymeric bonds, the polymeric layer is very thin, and no additional bonding is provided by the polymer outside the fiber crossing.

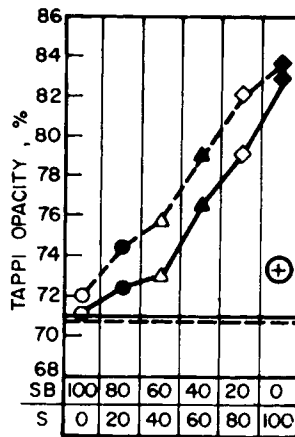
Second, the law of mixtures, often used for predicting the mechanical properties of composites is not applicable. The tensile strength of sheet is improved by a polymer that, on equivalent basis, has considerably lower strength than the untreated sheet.¹⁰

Third, the identity of the polymer is not decisively reflected in the mechanical properties of sheet. Concerning this point, it is of interest to consider the tensile strength and the elongation.

In Figure 6 a plot of the breaking length versus elongation at break for sheets containing 2, 5, and 10% latex of varying composition shows a direct relationship. On the right, the same plot for sheets containing 10% hard and soft latex mixed in various ratios and dried at room temperature also gives a straight line, but of



(a)



(b)

Fig. 5. Sheet properties as a function of 10% addition of mixtures of hard polystyrene (S) and soft styrene-butadiene copolymer (SB) latex. Sheets dried at room temperature (dashed line) and subsequently at 105°C for 5 hr (solid line). The single cross point indicates the change after heating at 150°C in a press (1 MPa \approx 10 atm) for 1 hr. The horizontal lines represent the properties of control sheets without latex, dried at room temperature (dashed line) and at 105°C for 5 hr (solid line).

lesser slope. As a higher temperature 105°C promotes the development of the full potential of the soft latex, the tensile strength increases proportionally with the content of the soft latex and the slope becomes steeper. A pressing at 150°C brings all the samples to similar values. The simultaneous increase in strength and elongation of a sheet in which direct interfiber bonds are substituted by polymeric bonds indicates a different mechanism of reinforcement from a system where polymer supplements the interfiber bonds. In the latter case, which can be approximated by impregnating a formed sheet with polymer dissolved in organic nonpolar solvent, it was shown⁸ that with rubbery polymers the elongation increases, with brittle polymers the strength is improved.

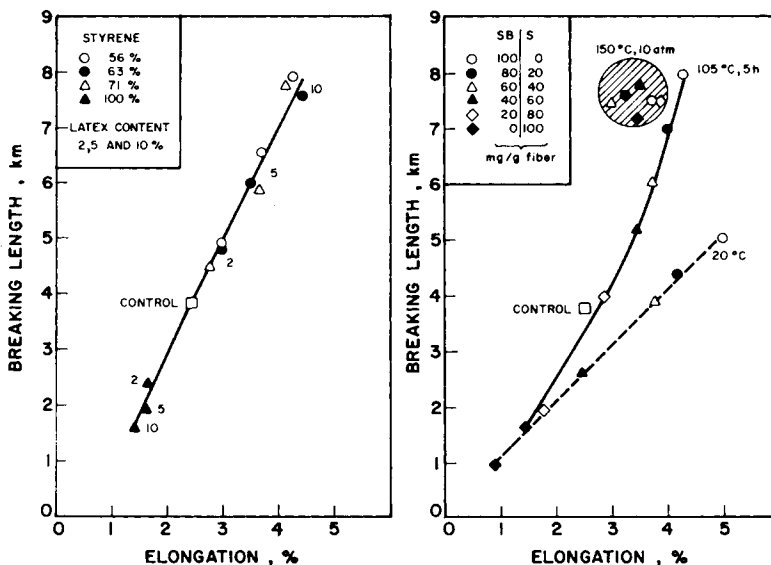


Fig. 6. *Left.* Breaking length vs elongation at break as a function of latex addition (2, 5, and 10% on fibers) and its composition (styrene content 56, 63, 71, and 100%). Sheets heated at 105°C for 5 hr. *Right.* Breaking length vs elongation at break of sheets with 10% latex mixture of hard polystyrene (S) and soft styrene-butadiene (SB) latex. Sheets dried at room temperature (dashed line) and subsequently at 105°C for 5 hr (solid line). Points in circle represent samples heated at 150°C in a press (1 MPa \approx 10 atm) for 1 hr.

Considering the overall behavior, it is suggested that the polymer acts as filler of the fiber's surface irregularities and thus provides a larger contact area between fibers and improved stress transfer between them. By increasing the temperature above T_g , a better accommodation of polymer is achieved, resulting in a further increase in contact area. As long as the polymer adheres to the fibers and is in a sufficient, but not excess, amount to fill the surface roughness, the mechanical properties of the polymer are of less importance in improving the bonding. This role is noticeable in case of unbeaten fibers, which have a limited number of direct interfiber bonds. Such bonds are active only over distances as short as a fraction of a nm, which, in the view of the roughness of the adjoining surfaces, is rarely achieved.

The suggestion that an increase in the bonded area is the main contribution of incorporated latex to improved strength is supported by comparing the surface areas of sheets treated with latex. In Table II the specific surface area measured by nitrogen adsorption shows a gradual decrease from the control sample without latex to a sheet containing 10% soft latex dried at room temperature and to a similar sheet subsequently heated at 105°C. The decrease in specific surface

TABLE II
Comparison of Specific Nitrogen Surface Area and Breaking Length^a

Characteristic	No latex control	10% Latex, no heat	10% Latex, 105°C, 5 hr
Surface area (m ² /g)	0.78	0.61	0.53
Breaking length (km)	3.7	4.4	6.9

^a These results are illustrative only because the samples differed from those used in the present experiments.

area indicates an increase in the bonded area, which is inaccessible to nitrogen molecules.

Another technique for evaluating the bonded area utilizes the measurement of optical properties, particularly light-scattering. In several studies,^{5,11-18} the relationship between the light-scattering coefficient and bonded area of paper has been demonstrated and exploited for studies showing the interdependence of paper strength and optical properties. In our case (Table II), the relationship between the surface area measured by nitrogen adsorption and the light-scattering coefficient is shown in Figure 7. As the surface area accessible to nitrogen decreases, i.e., increasing bonded area, the light-scattering coefficient decreases. Although the nitrogen surface area has been found to be linearly related to the light scattering, it should be realized that there is no absolute correlation. The optical contact determined by light scattering may not be identical to the molecular contact, in contrast with the probable correlation achieved with nitrogen adsorption. Two surfaces separated by a distance of a few nm are in optical contact, but too far apart for any kind of intersurface bonding to develop.

Figure 8 shows the light scattering coefficient as a function of the breaking length of sheets containing 2, 5, or 10% latexes of different softness or 10% latex mixtures of hard and soft latexes. The relationship indicates that the sheet reinforcement by latex is accompanied by a decrease in the light-scattering coefficient. That the relationship is not strictly linear is not surprising, considering the complexity of light scattering, particularly in a system containing three components. In the left-hand part of Fig. 8, two regions of linear dependency can easily be recognized: one above the control, where the sheet reinforcement is achieved by film-forming latexes; and the other below the control, where the weakening of the sheet is caused by nonfilming polystyrene latex. Here the loss of strength is accompanied by larger change in light scattering.

A possible reason for the dual dependency can be sought in the significant contribution of the hard latex to the total surface upon which light scattering takes place. The film-forming latex does not contribute to light scattering when spread on the fiber surface because it does not represent an additional surface. And since the indexes of refraction of styrene (1.59) and butadiene (1.52) are similar to that of cellulose (1.55-1.59), the polymer-fiber interface is virtually transparent with a scattering coefficient of zero. Therefore, the change in light scattering is probably affected mainly by the change in interfiber bonded area resulting from a filling of fiber's surface roughness by the polymer. When, in-

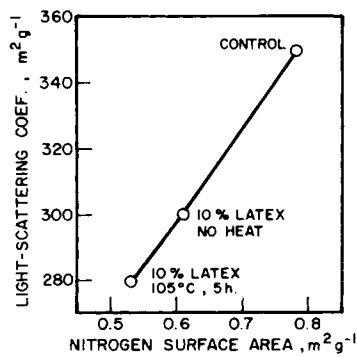


Fig. 7. Relation between nitrogen surface area and light-scattering coefficient.

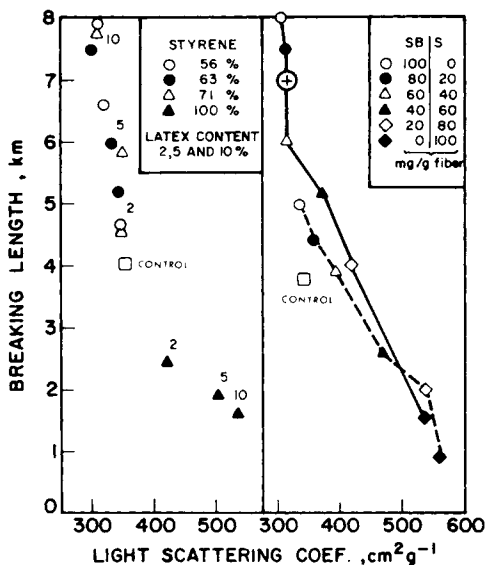


Fig. 8. Breaking length vs light-scattering coefficient as a function of latex addition (2, 5, and 10%) and its composition (56, 63, 71, and 100% styrene) for sheets heated at 105°C for 5 hr (*left*) and as a function of 10% latex mixtures of hard (S) and soft (SB) latex for sheets dried at room temperature (dashed line) and subsequently at 105°C for 5 hr (solid line) (*right*). The single cross point for the sheet with 10% hard latex heated at 150°C in press (1 MPa \approx 10 atm) for 1 hr.

stead of a filming latex, a hard latex is introduced, the fibers are prevented from forming a contact; this obviously increases the surface for light scattering. In addition, the latex particles provide a significant surface (ca. 40 m²/g latex) upon which scattering takes place, and, consequently, the debonding due to increasing amounts of hard latex is accompanied by more pronounced changes in the light-scattering coefficient.

The nonlinear dependence of breaking length and scattering coefficient in the right-hand part of Fig. 8 is probably the result of the complex effects of mixtures of hard and soft latex. The debonding effect and the additional surface of hard latex combine with the change in the bonded area affected by the film-forming latex. When the hard latex assumes the role of binder by heating above its T_g , the light scattering and breaking length become comparable to the values established for the soft polymers, as seen from the position of the cross point.

CONCLUSIONS

1. Cationic latex introduction into the sheet by wet-end addition under controlled conditions can result in replacement of fiber-fiber bonds by polymeric bonds.

2. The properties of sheets formed from unbeaten fibers are modified to a similar extent by film-forming latexes of different styrene-butadiene ratios, although the mechanical properties of the polymer films may differ considerably.

3. Hard polystyrene latex may perform similarly to film-forming latex, providing its good accommodation between fibers is assured. This can be achieved by heating the sheet above the polystyrene glass transition temperature supplemented by pressing.

4. Reinforcement of sheets formed from unbeaten fiber in which polymeric bonds substitute for direct fiber-fiber bonds is characterized by simultaneous increases of strength and elongation.

5. It is suggested that a probable mechanism of reinforcement is that the polymer acts as a filler of the fibers' surface irregularities, thus providing a larger contact area between fibers and improved stress transfer between them.

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